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INTERIM ENGINEERING REPORT NO. 3

INVESTIGATION OF LONG WAVELENGTH INFRARED GLASSES

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TABLE OF CONTENTS

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LIST OF TABLES

LIST OF FIGURES

A B S T R A C T

The purpose of this report is to present information on infrared transmitting glasses. This information consists of composition-property data obtained on glasses selected from the As-Se-Te field and investigation of new glasses with improved properties.

The program is divided into two parts. Iart I is a property measurement section to determine certain optical, thermal, and physical properties on 20 different glass compositions. These glasses have been selected from a collection of proprietary glasses consisting of combinations of As, Se, and Te. The glasses have been melted and property measurements have been completed or are in progress. These measurements include the following:

1. Infrared transmittance from 16 to 25 microns - completed.
2. Absorption coefficient from 2 to 25 microns - completed.
3. Refractive index and dispersion from 16 to 25 microns - in progress.
4. Anti-reflection coating evaluation from 8 to 14 microns - in progress.
5. Thermal shock resistance (MIL-E-0052720B Proc. 2) - in progress.
6. Resistance to nuclear radiation - in progress.

Part II consists of a composition study with the objective of developing new, improved glasses having transmittance to beyond 16 microns. This study uses the best glasses from Part I as a basis with substitutions of other elements in order to obtain additional glasses with improved infrared transmittance and greater thermal resistance (higher softening points).

1. INTRODUCTION

Considerable research effort has been expended in attempts to develop infrared optical materials suitable for use under environmental conditions. Although some measure of success has been attained in the development of materials transmitting in the near and intermediate wavelengths, there is at the present state-of-the-art no material which is entirely satisfactory for use in the far infrared.

Materials are urgently needed which combine good long wavelength transmission, particularly in the 8 to 13 and 12 to 25 micron bands, with adequate physical strength, thermomechanical properties, and reliability of performance. It is particularly desirable that such materials be glasses because of the comparative economy, ease of fabrication and versatility of glasses over other forms of material. Furthermore, glasses are capable of providing a wide range of refractive properties for the design of optical systems having wider fields of view and high resolving power.

This investigation is two-fold in nature: (1) to determine certain optical, thermal, and physical properties of glasses selected from the As-Se-Te field, and (2) to conduct a composition-property study on the addition and/or substitution of other elements in the As-Se-Te field. The substituent elements have been selected on the basis of probability of glass formation and predicted long wavelength cutoff determined by the application of solid state physics principles.

2. DISCUSSION

This section describes the results achieved thus far on this program. It is divided in two parts in conformance with contract planning.

2.1 Part I

This is essentially a property measurement section designed to determine certain optical, thermal, and physical properties of 20 different glass compositions. The final selection and melting of these glasses was completed under ONR Contract No. NOnr 3647(00) Project Defender, sponsored by the Advanced Research Projects Agency and administered by the Office of Naval Research. Considerable property data were shown in the ONR final report.

Transmittance measurements on all 20 glasses for two thicknesses have been completed over the wavelength range from 16 to 40 microns. This is broader than the originally scheduled 16 to 25 micron range. The additional data were obtained through the use of a spectrophotometer which covers the IR to 40 microns without substantially increasing the measurement complexity or time and effort.

All of the glasses show decreasing transmittance starting at about 18 microns with a large absorption band centered at approximately 22 microns. Complete data on all 20 glasses will be presented in the final report. A typical curve on glass 62-73B is drawn in Figure 1, attached.

From the transmittance on two samples of glass of different thickness the absorption coefficient was calculated from the following formula:

$$\alpha = \frac{2.3}{x_1 - x_2} \log_{10} \frac{i_2}{i_1}$$

where α = absorption coefficient in cm^{-1}

x_1 = thickness of sample 1 in cm

x_2 = thickness of sample 2 in cm

i_2 = transmittance of sample 2

i_1 = transmittance of sample 1

Values from 2 to 25 microns are shown in Table 1. The two samples of each glass were approximately 2 and 8.8 mm for the calculated coefficients.

Calibration of the KBr prism optics on the infrared refractometer was completed and measurements attempted on one of the glass prisms. Considerable difficulty was encountered because of weak readout signals beyond 16 microns. This problem is engendered by the absorption of the sample and decrease in source intensity as longer wavelengths are imposed. A complete re-evaluation of the electro-optical set-up is being made to ascertain to what extent measurements beyond 16 microns are feasible. At this time, it appears that measurements of refractive index at selected wavelengths from 16 to 25 microns might be possible.

Various anti-reflection coatings are being considered for use with selected glasses. Three glasses with indices of 2.66, 2.81, and 3.12 are being melted in sufficient quantities to prepare samples for coating tests.

A rack for holding thermal shock specimens was constructed. Samples will be 1/4" thick by 2" diameter and will be subjected to thermal cycling according to MIL-E-005272B, Procedure 2.

The 20 glass samples are in the process of being exposed to radiation from a Cobalt 60 source. Infrared transmittance measured before and after exposure will indicate the resistance of the glasses to nuclear radiation.

2.2 Part II

The high temperature melting furnace was received and placed in operation. The control and power supply circuits were checked out and perform satisfactorily. Several heating and cooling cycles were repeated to dry out and fire the refractory parts. Several melts were made at 800° C with satisfactory performance of the furnace.

A technique was developed to encapsulate glass melts in fused quartz tubes. This allows us to subject the melts to higher temperatures which is desirable in working with the new materials which have higher melting points.

Melt No. 62-110B was crushed up and vacuum sealed into a quartz envelope using this new procedure. This melt had previously shown about 50-50 glass crystal after melting at 600° C in a Pyrex envelope. After sealing in quartz, the glass was melted at 800° C for one hour and cooled in place at the normal furnace cooling rate. Microscopic examination of this melt did not reveal any crystal formation or unmelted batch as displayed by the 600° C melt. This fused SiO_2 technique when used on 10 mm tubes does not produce samples large enough for transmission tests which require a 1 inch disc. The small 10 mm diameter by 1" long piece was slumped

into a mold at 400° C to produce a disc about 1/8 inch thick and 1" diameter. This piece was then ground and polished to obtain a transmission sample. The transmittance and composition of melt 62-110B are shown in Figure 2. The absorption band at 12.8 microns is typical of As-Se combinations and persists in this glass also. However, the transmittance from 2-11 microns looks promising. Additional melts using the fused SiO_2 envelope technique will be described later.

Two other melts were made in 100 gm quantities in Pyrex under vacuo at 600° C. The original 10 gm melts on these compositions showed considerable promise but no properties were measured because of the lack of sufficient glass. These are shown in Figure 2 as melts 95 and 96. Note that these glasses contain 5 and 10% germanium. Glasses 95 and 96 again display the 12.8 micron absorption band but have good transmittance from 2-11 microns. In examining the transmission specimens it was noticed that the samples are transparent to visible light showing a dark ruby color. This is somewhat surprising in view of the opacity of As-Se glasses containing the metal additions. It is felt that the 12.8 micron absorption band can be reduced by proper heat treatment since this has been done with As-Se glasses without germanium. This approach will be considered.

The physical characteristics of glasses 62-95 and 62-96 seem to be improved with Ge addition. The glasses are definitely less fragile and much easier to grind and polish than glasses composed of As-Se-Te.

Thermal expansion was measured on these glasses. A comparison with the properties of As_2Se_3 follows:

Composition Wt. %	As_2Se_3	62-95	62-96
As	38.7	34	29
Se	61.3	61	61
Ge	-	5	10
Critical Point, °C	183	196	215
Softening Point, °C	202	232	258
Thermal Exp. X 10^{-6}/°C	18.6	18.0	16.8

From these data, it appears that the substitution of Ge for As increases the softening point and lowers the thermal expansion. This is in the direction anticipated. The quality of these glasses indicates compatibility of Ge in the As-Se glass field.

A total of 17 glasses composed of As-Se-Ge were melted to determine composition field limits. Figure 3 shows a ternary plot of the compositions selected along with As-Se base glasses. A complete investigation of this composition field is underway to determine the limits of glass formation, thermal properties, and IR transmittance. Table 2 is a compilation of the data obtained to date. The transmittance was measured on those glasses which appeared to have good glass forming qualities as judged by visual examination. Transmittance is good except for a broad absorption band at 12-13 microns. Glass No. 62-144B is typical of the series. This is illustrated in Figure 4.

All the glasses in Table 2 were melted at 625° C in Pyrex tubes in vacuo except numbers 144, 145, 146 and 147. The temperature was raised to 700° C on these melts but the

Pyrex tubes collapsed indicating the need for fused quartz encapsulation tubes to allow higher melting temperatures.

Larger fused quartz tubes were purchased which made it possible to melt quantities large enough for property measurements. Four of the glasses which exhibited unreacted batch when melted in Pyrex were re-melted in fused quartz envelopes, in vacuo, at 800° C. At this temperature the molten glasses were very fluid and stirring was accomplished by tilting the tube back and forth to allow the materials to react completely and homogenize. This procedure was followed to obtain specimens of glass which were then evaluated for quality and other properties. These data are tabulated in Table 3. Note the marked improvement in thermal properties of 62-137BR-1, which contains 25% Ge substituted for As.

As a result of the melts made with As-Se-Ge combinations, it appears that considerable improvement in glass quality has been achieved with Ge additions. Samples for transmittance measurement were ground and polished with comparative ease showing very little tendency to chip at the edges as experienced with As-Se-Te glasses. Softening point has been raised considerably with an attendant decrease in thermal expansion. In view of these results it seems desirable to pursue this composition field more thoroughly to ascertain the limits of glass formation and property benificiation.

3. RESULTS AND CONCLUSIONS

3.1 Part I

3.1.1 In general, all 20 glasses show transmittance beyond 16 microns to decrease starting at about 18 microns with a large absorption band centered in the vicinity of 22 microns.

3.1.2 Absorption coefficients increase at longer wavelengths beyond 16 microns demonstrating that the decreased transmittance is due to internal absorption by the glasses.

3.1.3 Measurements on the infrared refractometer have shown that determinations at selected wavelengths from 16 to 25 microns might be feasible.

3.2 Part II

3.2.1 The high temperature melting furnace was used successfully to melt glasses in fused quartz envelopes at 800° C.

3.2.2 Glasses melted at 800° C display a considerable upgrading in quality, homogeneity, and stability when compared with melts made at 600° C.

3.2.3 The physical characteristics of As-Se glasses are greatly improved by the addition of germanium. The glasses are less fragile and easier to grind and polish.

3.2.4 Substitution of Ge for As in As-Se glasses increases the softening point and lowers the thermal expansion.

4. RECOMMENDATIONS

4.1 Measurements of refractive index should be restricted to wavelengths of high transmittance in the region of 16 to 25 microns.

4.2 All future evaluation glass melts should be made in fused quartz tubes at elevated temperatures to ensure complete vitrification.

4.3 A complete composition-property study of the As-Se-Ge glass field should be made to ascertain the limits of physico-optical characteristics.

4.4 Additional additives to As-Se and/or As-Se-Ge glasses should be incorporated when the glasses are melted at elevated temperatures to examine these other glass composition fields for range of property versatility.

TABLE 1 - ABSORPTION COEFFICIENTS OF 20 SELECTED GLASSES

Wavelength - Microns

GLASS	2	3	4	5	6	7	8	9	10	11	12	13	14	15
62-73B	0.7	0.5	0.5	0.5	0.6	0.6	0.6	0.6	0.7	0.7	0.7	1.0	1.7	2.9
62-74B	1.2	1.5	1.9	1.[illegible]	1.5	2.0	2.0	2.1	2.1	2.2	2.2	3.4	3.4	3.8
62-75B	1.4	0.5	0.2	0.2	0.2	0.2	0.3	0.3	0.3	0.4	1.7	4.3	3.0	2.5
62-76B	0.5	.7	0.5	0.5	0.5	0.5	0.6	0.6	0.6	0.6	1.4	7.6	1.6	2.3
62-77B	0.4	0.2	*	*	*	*	*	*	0.1	0.1	0.6	2.7	1.2	2.0
62-78B	0.5	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.5	0.8	1.0
62-79B	*	*	*	*	*	*	0.1	0.1	0.1	0.2	1.0	4.0	1.9	2.5
62-80B	1.0	0.5	0.2	0.1	*	*	0.1	0.1	0.1	*	0.5	3.1	0.9	1.4
62-81B	*	0.1	0.1	0.1	*	*	0.2	0.2	0.2	0.1	0.8	3.4	1.4	2.2
62-82B	1.7	1.4	0.8	0.6	0.4	0.4	0.5	0.4	0.5	0.5	2.0	4.7	3.1	3.6
62-83B	0.5	0.7	0.3	0.2	0.2	0.2	0.2	0.3	0.3	0.3	0.3	1.0	1.2	2.5
62-84B	0.3	0.4	0.3	0.3	0.2	0.3	0.3	0.3	0.3	0.3	0.7	1.5	1.3	1.5
62-85B	0.2	0.2	0.2	0.1	0.2	0.2	0.2	0.2	0.2	0.2	0.4	2.6	1.0	1.5
62-86B	0.1	0.2	0.1	0.1	0.1	0.1	0.1	0.1	0.2	0.2	0.3	1.0	0.8	1.2
62-87B	0.4	0.5	0.5	0.5	0.6	0.6	0.6	0.7	0.7	0.8	0.8	2.1	2.1	3.6
62-88B	*	*	0.1	0.1	0.1	0.2	0.2	0.3	0.2	0.2	0.4	2.4	1.7	3.0
62-89B	0.2	0.3	0.4	0.3	0.3	0.4	0.3	0.4	0.4	0.4	0.5	2.2	1.4	2.7
62-90B	0.1	0.1	*	*	*	*	*	0.1	*	*	0.3	0.9	0.7	1.6
62-91B	*	*	*	*	0.1	0.1	0.1	0.2	0.1	0.2	0.3	1.4	0.7	1.6
62-92B	0.3	0.3	0.3	0.2	0.2	0.2	0.3	0.3	0.3	0.3	0.7	2.1	1.3	1.7

* less than 0.05

WAVELENGTH - MICRONS

GLASSES	16	17	18	19	20	21	22	23	24	25
62-73B	2.2	2.1	2.1	3.5	2.0	1.4	1.4	1.4	2.0	2.5
-74B	3.5	2.9	2.7	1.7	**	**	1.0	3.7	4.5	4.4
-75B	.2	2.6	2.3	2.4	2.6	1.6	1.6	2.6	3.4	3.5
-76B	2.3	1.8	1.6	2.0	2.5	2.0	2.0	2.0	2.0	2.1
-77B	2.0	1.4	1.3	2.5	3.1	3.2	3.0	3.0	3.2	3.4
-78B	.7	.6	.9	1.8	1.4	.4	1.6	2.3	3.1	3.3
-79B	1.4	2.7	2.0	2.7	1.9	1.6	1.6	1.6	2.2	2.6
-80B	1.9	1.4	1.2	1.6	2.9	1.6	2.4	2.6	3.0	3.0
-81B	1.6	*	.4	2.3	**	**	0.6	2.3	2.9	2.9
-82B	1.5	2.5	2.8	2.6	1.2	**	**	**	**	1.6
-83B	1.8	1.5	1.5	2.4	1.8	1.0	1.0	1.0	2.0	2.4
-84B	.2	1.4	1.2	2.1	3.3	3.4	2.6	2.6	2.9	3.0
-85B	1.9	.8	.9	2.1	2.3	2.1	2.0	2.5	2.5	2.6
-86B	.9	.8	1.2	2.5	1.7	1.0	1.0	2.7	3.4	3.4
-87B	2.1	2.1	1.8	2.2	1.0	**	1.0	2.6	3.7	5.7
-88B	1.7	1.5	1.5	1.8	**	1.0	1.0	1.6	3.4	3.7
-89B	2.1	1.6	1.6	2.4	1.3	1.0	1.6	2.0	3.1	3.5
-90B	.9	.8	.8	1.3	.4	1.0	2.1	1.0	3.9	4.2
-91B	.5	.8	.8	1.4	2.4	2.2	3.0	3.0	3.2	3.6
-92B	1.7	1.6	1.3	2.2	1.9	.8	1.8	2.3	2.8	3.4

** indeterminate - transmittance values too low

TABLE I - ABSORPTION COEFFICIENTS OF 20 SELECTED GLASSES
(cont'd.)

TABLE 2

PROPERTIES OF As-Se-Ge GLASSES MELTED IN PYREX, IN VACUO, AT 600° C

MELT NO.	WT. % As	WT. % Se	WT. % Ge	RESULTS 100 gm. MELTS	THERMAL EXP. X10^{-6}/° C	CRITICAL POINT, °C	SOFTENING POINT, °C
62-99B2	39	56	5	Glassy			
62-100B2	39	51	10	"	20.9 (25-125)	210	245
62-134B	39	46	15	Incomplete melting			
62-135B	24	61	15	" "			
62-136B	19	61	20	Unreacted batch			
62-137B	14	61	25	" "			
62-138B	22.5	72.5	5	Glassy, large bubbles			
62-139B	17.5	72.5	10	" " "			
62-140B	12.5	72.5	15	Unreacted batch	21.1 (25-125)	145	207
62-141B	15	80	5	Glassy	35.9 (25-125)	102	143
62-142B	10	80	10	Incomplete melting			
62-143B	35	50	15	" "			
62-144B	30	50	20	Glassy	14.4 (25-225)	260	340
62-145B	50	45	5	Glassy	24.2 (25-200)	205	255
62-146B	45	45	10	"	17.1 (25-200)	220	295
62-147B	50	50	-	Glassy, large bubbles			

TABLE 3

Remelts of As-Se-Ge Glasses Made in Fused Quartz Tubes, In Vacuo, at 800° C. Quench Temperature 260° C.

MELT NO.	WEIGHT % As	WEIGHT % Se	WEIGHT % Ge	MELTING TIME HRS	RESULTS*	THERMAL EXP. $X10^{-6}$/°C (25-225° C)	CRITICAL POINT, °C	SOFTENING POINT, °C
62-136BR-1	19	61	20	16	1	16.8	247	310
62-137BR-1	14	61	25	16	2	14.7	290	347
62-142BR-1	10	80	10	5	3	Not determined - incomplete melting		
62-143BR-1	35	50	15	5	4	16.4	257	294

*Results

1. Deep red, transparent glass. Good quality, some striae, few bubbles.
2. Deep red, transparent glass. Good quality, striae free, very few bubbles.
3. Black, opaque glass, many large bubbles throughout.
4. Very dark red, transparent glass. Heavy striae, very few bubbles.

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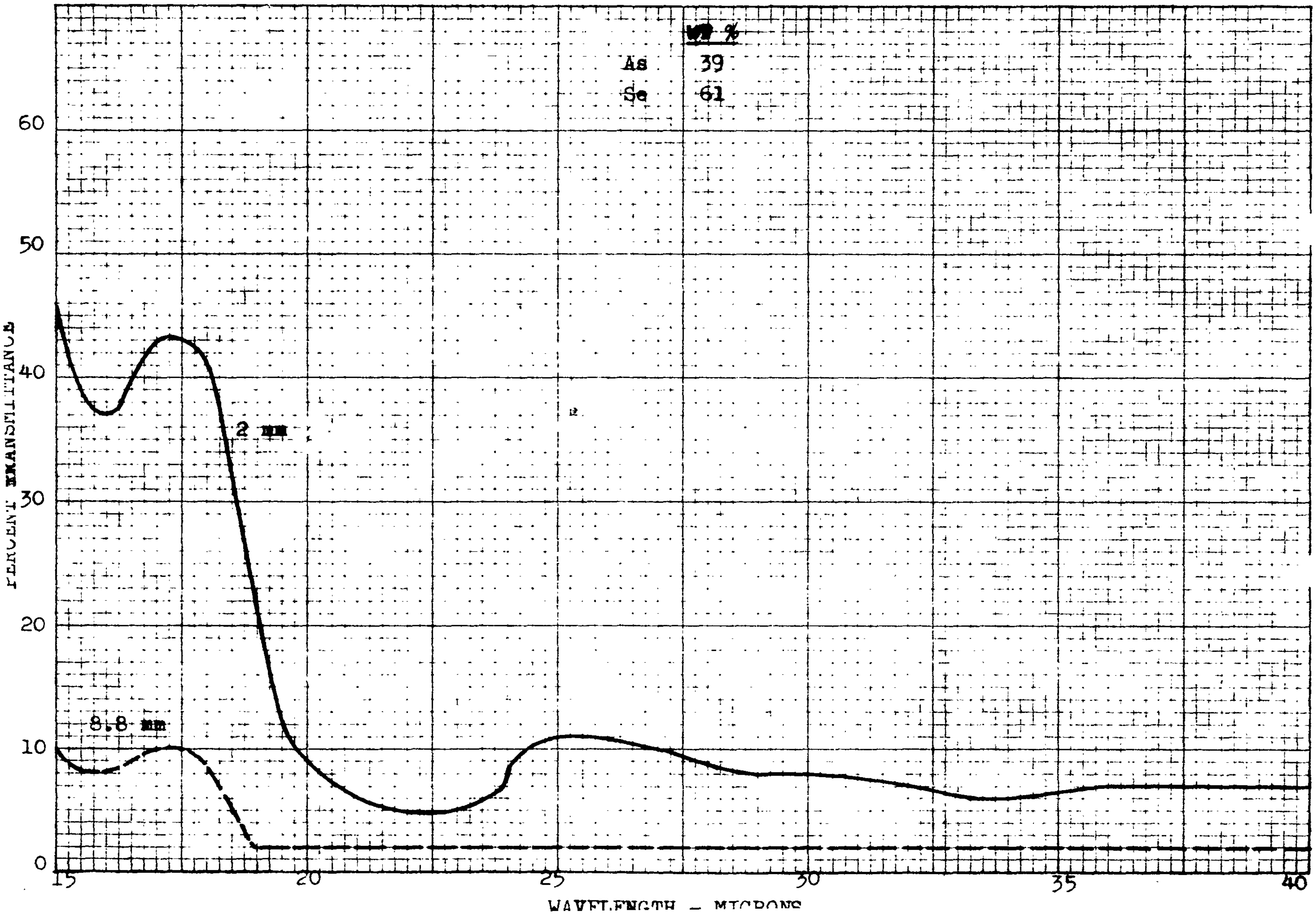
FIGURE 1 - IR TRANSMITTANCE OF GLASS NO. 62-73B



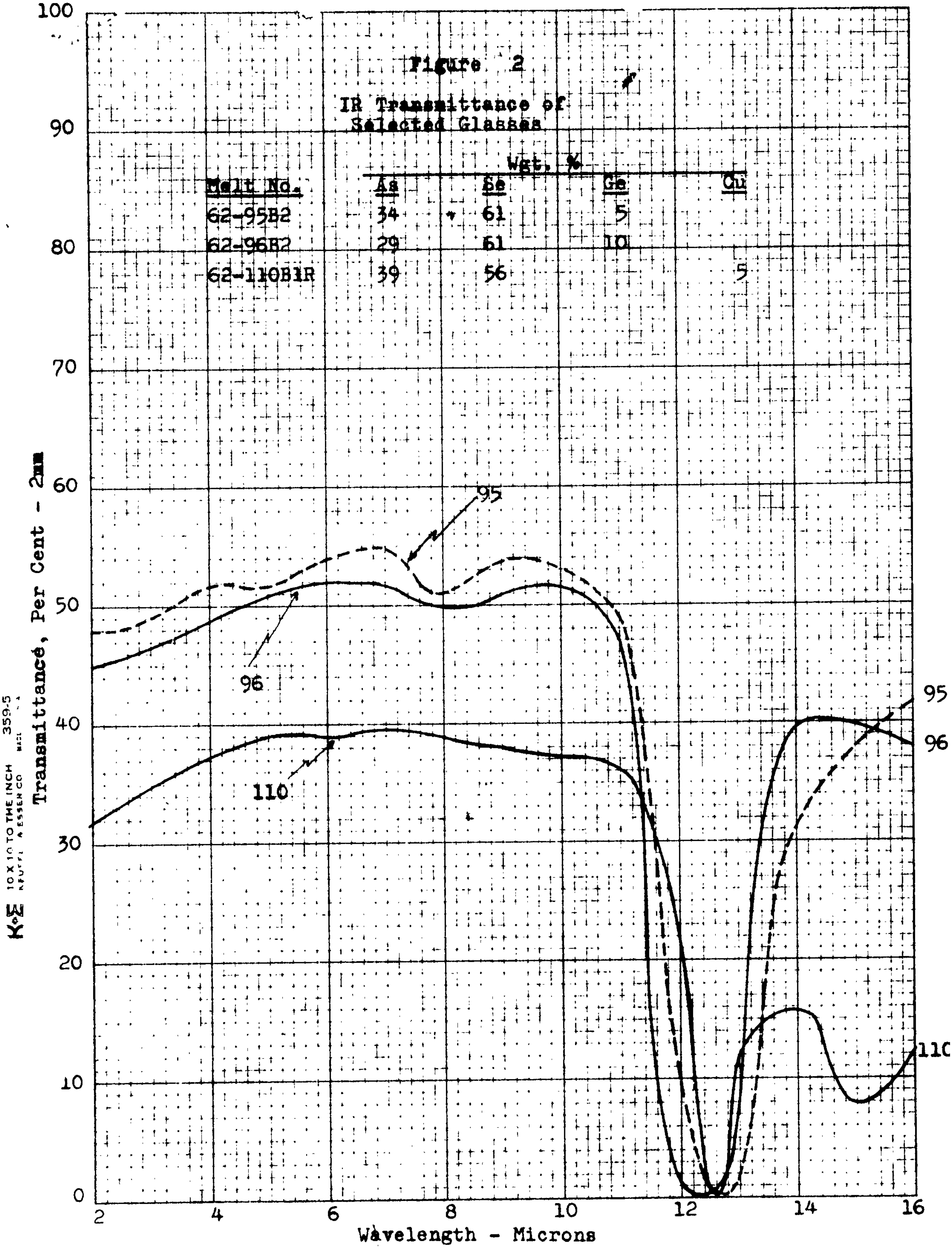


Figure 2
IR Transmittance of Selected Glasses
Wgt. %
Melt No.
As
Se
Ge
Cu
62-95B2
34
61
5
62-96B2
29
61
10
62-110B1R
39
56
5
95
96
110
95
96
110
Transmittance, Per Cent - 2mm
Wavelength - Microns
100
90
80
70
60
50
40
30
20
10
0
2
4
6
8
10
12
14
16
K+E 10 X 10 TO THE INCH 359-5
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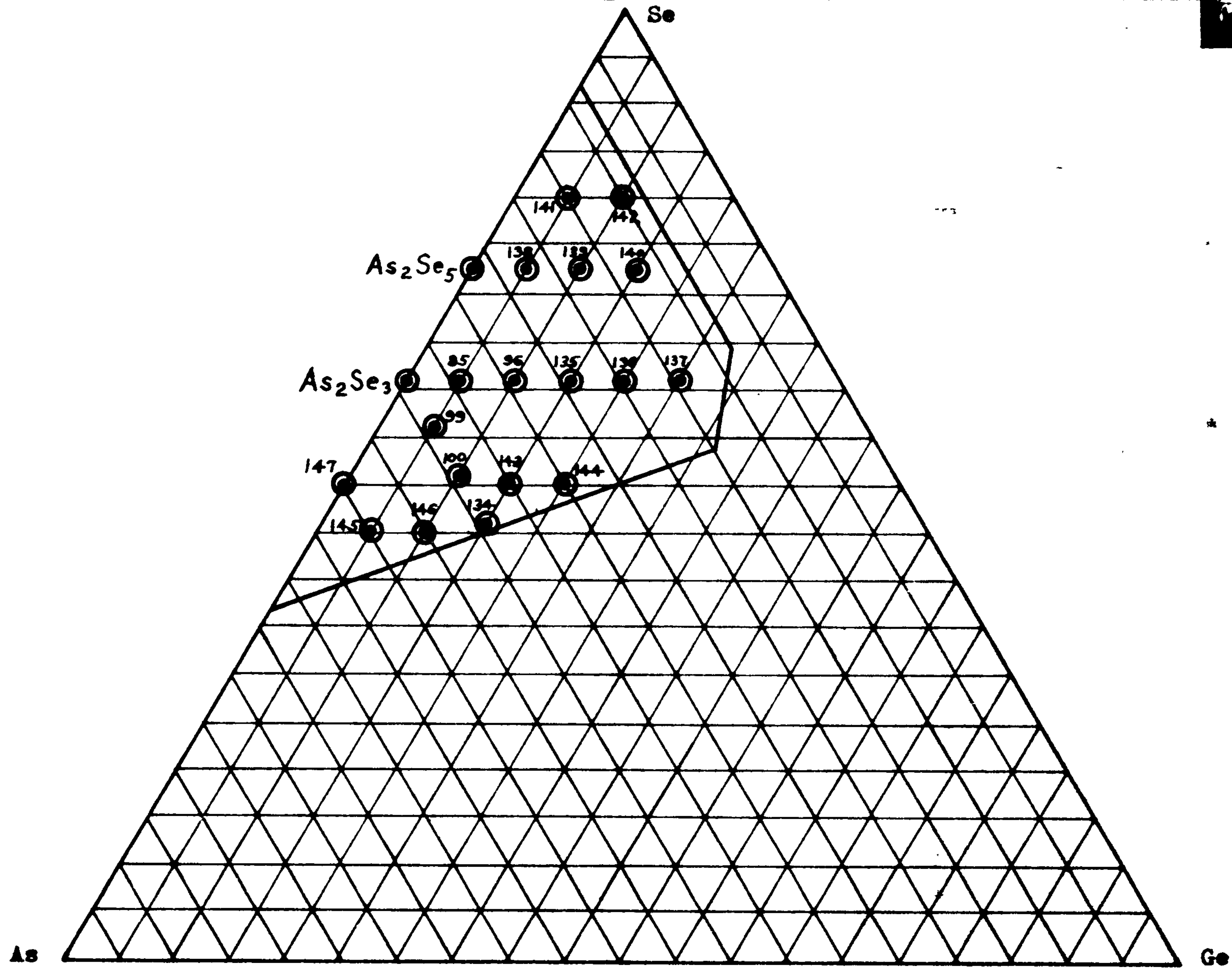

FIGURE 3 - As-Se-Ge COMPOSITION FIELD

FIGURE 4- IR TRANSMITTANCE OF GLASS NO. 62-144B, 2mm THICKNESS